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SHOCK TUBE DECOMPOSITION OF NITROUS OXIDE

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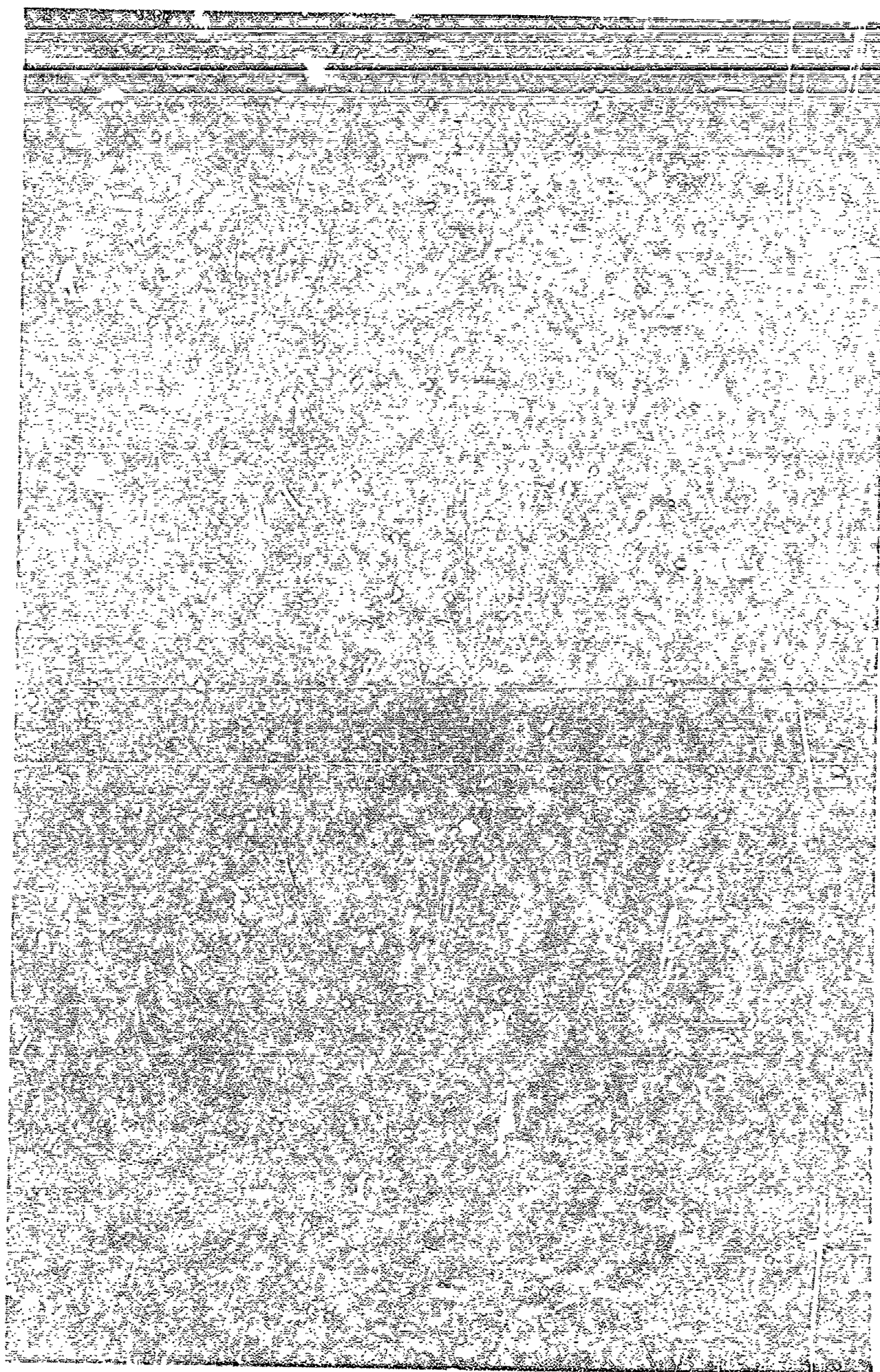
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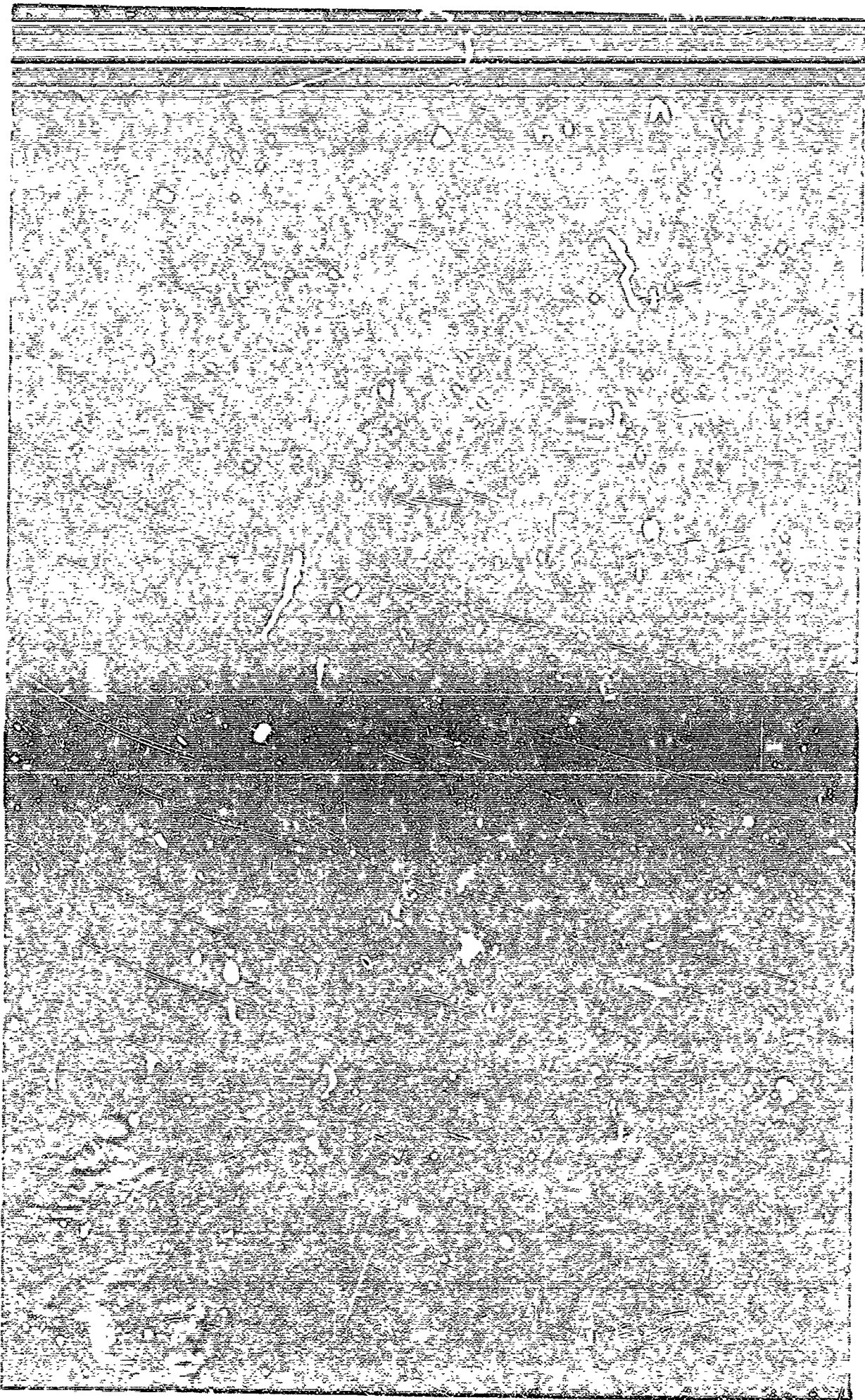
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SHOCK TUBE DECOMPOSITION OF NITROUS OXIDE

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/
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FOREWORD

This interim technical documentary report was prepared by E. Stokes Fishburne, Daniel M. Bergbauer, and Rudolph Edse of the Department of Aeronautical and Astronautical Engineering of The Ohio State University on Contract Number AF 33(657)-8951, Project 7064, Aerospace Simulation Techniques Research, Task 7065-01, Fluid Dynamics Facilities Research. The research on this task was administered under the direction of the Aerospace Research Laboratories, Office of Aerospace Research, United States Air Force, with Mr. John Goresch, Fluid Dynamics Facilities Laboratory, as Contract Monitor.

This report covers one phase of the investigation on Contract AF 33(657)-8951.

ABSTRACT

The thermal decomposition of nitrous oxide has been studied in the temperature region from 1500°K to 2200°K. At temperatures higher than 2200°K the rate of decomposition is too rapid for accurate measurements. Shock tube techniques, employing the region behind the initial shock wave, were used. Because of the exothermic nature of the decomposition of nitrous oxide it was necessary to study mixtures of nitrous oxide in an excess of diluent. The gases normally used as diluents were argon, nitric oxide, oxygen, and air. In general, the concentration of nitrous oxide was 2% by volume with 98% diluent.

The results obtained with nitric oxide as a diluent indicate that the reaction is bimolecular. The rate constant derived from these experiments is in excellent agreement with the rate constant obtained by other investigators at lower temperatures.

The data obtained with argon, oxygen, or air as diluents indicate that the decomposition is bimolecular at low concentrations and becomes monomolecular at higher concentrations. The high concentration limit was not reached in this study.

There is good agreement between the data obtained in this study and the data obtained by other investigators at lower temperatures. However, the activation energy was found to depend on concentration. The maximum activation energy occurs at the highest total concentration, about 1.50×10^{-4} moles/cc, and was determined to be 56,000 cal/mole.

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LIST OF SYMBOLS

(C)	Concentration of the radiating species
$(C)_0$	Initial concentration of species i behind the shock wave
t	Time
t_L	Laboratory (oscilloscope) time
E_{act}	Activation energy
E_∞	Activation energy at high concentration limit
ϵ	Energy level from which species i radiates
T	Absolute temperature
v	Vibrational quantum number
θ_v	Characteristic temperature of particular vibration-rotation band v
Q	Partition function
α	Fractional amount of species i which has decomposed
k_j	Reaction rate constant for reaction j
K_{exp}	Experimental reaction rate constant based on first order reaction
M	Inert species
ρ	Density
ρ_0	Initial density behind the shock wave
I	Intensity at any time t
I_0	Initial intensity
R	Universal gas constant
A	Frequency factor

SECTION I

INTRODUCTION

The laboratory simulation of very high Mach number flows on a continuous basis in a wind tunnel has been hindered somewhat by the temperature to which the air may be heated. Conventional electrical heaters can be used only to about 2300 to 2500° Fahrenheit and consequently when the flow is expanded greatly, the gas may condense. Other types of heaters have been proposed, such as the pebble-bed heater and the carbon heater. However, both of these suffer from various limitations. The most noteworthy limitation is the oxidation of the surface by the hot oxygen. The possibility of using nitrous oxide as part of the working fluid in a wind tunnel has been discussed in other reports in the literature (Ref. 1-3). In general these reports have considered the overall aspect of the nitrous oxide addition. In particular the report by Thomas (Ref. 3) describes an attempt to heat the nitrous oxide by conventional electrical heaters. However, considerable difficulty was experienced since the nitrous oxide tended to decompose in the eddying flow behind the electrical heaters. In the very localized decomposition the heat of the decomposition was transferred to the heaters and resulted in a burn-out of the heater. Other possibilities of using nitrous oxide exist but these will be discussed in a later report. At the present time we are primarily interested in trying to determine the rate at which nitrous oxide decomposes at very high temperatures and pressures.

Johnston (Ref. 4) presents a complete survey of all low temperature data concerning the decomposition rate of nitrous oxide. The maximum temperature obtained in these experiments was 1052°K. The experiments described in Ref. 4 for the most part were conducted in constant volume devices. The description of the apparatus may be obtained in Ref. 5 and 6. However, to study the high temperature thermal decomposition of nitrous oxide these constant volume devices could not be used because of the rapid increase in the decomposition rate. Several other reports have been presented which include data in the temperature region between 1500°K and 2200°K (Ref. 7, 8 and 12). Fishburne et al (Ref. 7) present data collected in a shock tube for a mixture of nitrous oxide and argon. Bradley and Kistiakowsky (Ref. 8) present data also collected in a shock tube but this data is somewhat questionable in that they were trying to prove the merits of a particular high speed sampling system. A further point of question is that they used the reflected shock wave in a shock tube with an inside diameter of only 1/2 inch. It has been shown by Strehlow and Cohen (Ref. 9) and Skinner (Ref. 10) that the condition behind the reflected shock wave is somewhat questionable due to the interactions between the boundary layer and the reflected shock wave. This phenomena also is discussed by Mark (Ref. 11).

The only other data obtained at high temperatures are the experimental data obtained by Jost et al (Ref. 12) in which they studied the rate of decomposition of nitrous oxide in an excess of argon. However, these authors also used the reflected shock wave in the shock tube.

The experiments to be described in this report present experimental data on the rate of decomposition in argon-nitrous oxide, nitric oxide-nitrous oxide, oxygen-nitrous oxide, and air-nitrous oxide mixtures. These experiments were conducted in a shock tube, to be described, and the data were obtained behind the incident shock wave thereby removing the problem of the uncertainty of the conditions behind the reflected shock wave. The experimental arrangement will also be discussed since a knowledge of experimental techniques is pertinent in the final discussion concerning the possible sources of error.

SECTION II

EXPERIMENTAL APPARATUS

The use of a shock wave to generate high temperatures for the study of very fast reactions has been discussed elsewhere, in particular Ref. 7, 13, and 19. The shock tube used in this study consists of two sections: 1.) a driver section, which is 17 feet long with a 3 inch inside diameter, 2.) a driven section, which is 19 feet long with a 3 1/2 inch inside diameter. Both sections are constructed of stainless steel. A dump tank is located at the end of the driven section to increase the time required before the shock wave reflects from the end of the tube and returns to the region where the gas is being studied. For a detailed description of this shock tube the reader is referred to Ref. 7. The shock wave is generated by bursting a diaphragm placed between the two sections. The diaphragm is ruptured by increasing the driver pressure. In general, the increase in pressure in the present arrangement was obtained either by the combustion of the gas or by injecting gas from a very high pressure reservoir. The driver section is equipped with 17 low voltage ignitor probes spaced about 18 inches apart and staggered on either side. The power supply for the ignitor probes consists of a 6 volt wet cell battery. This battery is used to explode pyrofuze ignitor wires which in turn ignite the combustible mixture. Measurements of the time required to ignite 10 probes indicate that the total time involved is less than about 8 milliseconds. This short ignition time should assure a fairly uniform combustion.

The diaphragms used in the experiments were either made of mylar or of cold rolled steel, which had been scribed to provide a uniform rupture. The metal diaphragms were generally used with the combustion system and the mylar diaphragms were used for the high pressure system when hydrogen was used as the driver gas. Frequently, however, mylar also was used with the combustion arrangement.

A. Velocity Measurement

The velocity of the shock wave was measured at several points on the tube to provide information on its attenuation. In general, it was found that the attenuation with a hydrogen driver was negligible; whereas with the combustion driver, it was not negligible in some cases. The shock wave

velocity was determined by measuring the time of passage of the shock wave between two sets of platinum strips. The resistance of the platinum strips increases when subjected to a temperature increase. The initial change of the resistance will occur in less than one microsecond, thereby providing a rather accurate check of the time of passage of the shock wave. These platinum strips can be used for 50 to 80 experiments.

In order to construct a thin film platinum element, a thin platinum film must be adhered to a nonconductive base. For these bases both pyrex and quartz are suitable. Once the platinum, in the form of platinum particles suspended in a liquid, is applied to pyrex the glass must be baked in an oven to fuse the platinum to the glass. The resistances obtained in this manner were of the order of 300 ohms. A typical arrangement of the platinum strip is shown in Figure 1. The end of the pyrex is flush with the tube wall in order that the flow of the gas will not be disturbed. The platinum strip is placed in one arm of an electrical bridge. Thus, when the resistance of the platinum strip changes due to the arrival of the shock wave, a change in the voltage drop across this strip is obtained. This change in voltage drop is then amplified and used as the timing pulse. A schematic diagram of the amplifiers used in this arrangement is shown in Figure 2. The output from the amplifiers is then directed into a ten megacycle chronograph. The pulse from the first detector is used to start the unit counting and the pulse from the second detector, spaced 0.5 meters away is used to stop the unit. The shock wave velocity is calculated by dividing the distance traveled by the wave by the time required to travel the prescribed distance. Generally, the accuracy of this timing device is about 0.5 microseconds. In an overall time of 300 microseconds, this represents an accuracy of about 0.2% in the calculation of the shock wave velocity.

At a point slightly further down the tube the shock wave velocity is measured again. This second measurement occurs just before the point at which the decomposition is studied. This measurement provides an accurate knowledge of the exact shock wave velocity at the time of arrival of the shock wave at the observation point. A differentiated form of the output from two platinum strips is displayed on an oscil scope on which is superimposed a ten microsecond timing pulse. A typical photograph of the oscilloscope trace is shown in Figure 3. The measurement of the time of passage of the shock wave from this photograph is felt to have an accuracy of about microsecond in 300 or about 0.3%.

B. Calculation of Temperature and Pressure Behind the Shock Wave

The method whereby the thermodynamic state of the gas behind the shock wave is determined, is discussed in Ref. 7. Briefly, it is assumed that the gas is in complete thermodynamic equilibrium. The enthalpy of the mixture is determined on a percentage basis from the known composition of the sample mixture. The conditions behind the shock wave are presented in graphical form from which, for a given shock wave velocity, the thermodynamic variables may be determined.

C. Determining the Rate of Decomposition of Nitrous Oxide

To determine the rate of decomposition of nitrous oxide it was decided to use spectroscopic methods. Spectroscopic methods have an advantage in that it is not necessary to insert probes into the mixture to determine the rate of decomposition of a particular species. In particular, the time rate of change of the concentration of nitrous oxide was determined by observing the infrared radiation from nitrous oxide. When this gas is heated it radiates in certain spectral regions in the infrared (Ref. 14). In this study the radiation at 4.5 microns and at 3.9 microns was monitored to determine the rate of decomposition. The intensity of radiation of the heated gas may be given by

$$I = \frac{\text{const. } (C) \exp(-\epsilon/RT)}{Q} \quad (1)$$

where (C) is the concentration of the radiating species, ϵ is the energy level from which the species are radiating, and Q is the partition function. In the infrared region of interest, the primary gas radiation is due to the vibration-rotation bands of the molecules. For the 4.5 micron band the equation above reduces to

$$I = (\text{const.}) (C) \exp\left(-\frac{1}{2} \frac{\theta_1}{T}\right) \exp\left(-\frac{\theta_2}{T}\right) \left(1 - \exp\left[-\frac{\theta_3}{T}\right]\right) \exp\left(-\frac{\theta_3}{T}\right) \quad (2)$$

$$Q_1^{-1} Q_2^{-2}$$

where θ_3 is the characteristic temperature of the 4.5 micron vibration-rotation band and Q_1 and Q_2 are the partition functions for θ_1 and θ_2 respectively. From the last two equations we find that the intensity of the radiation is directly proportional to the concentration of the species (C) and the effect of vibrational temperature of the particular vibrational mode of interest. If there is an appreciable change in the temperature and pressure as the reaction proceeds, then there will be an appreciable change in the concentration of the species due primarily to the change in temperature, pressure, and the decrease in the concentration due to chemical reactions. We may write for the change in species concentration

$$(C) = (C)_0 \frac{\rho}{\rho_0} (1 - \alpha) \quad (3)$$

where ρ_0 is the initial density behind the shock wave, $(C)_0$ is the initial concentration of the species behind the shock wave, and α is the fractional

amount which has disappeared during the reaction. In other words if 75% of the initial amount has disappeared then α equals 0.75. Substituting this expression into the last equation for the intensity produces

$$I = (\text{const.})_2 \left(\frac{\rho}{\rho_0}\right) (1 - \alpha) (1 - \exp [-\theta_3/T]) Q_1^{-1} Q_2^{-2} \exp \left(-\frac{1}{2} \frac{\theta_1}{T}\right) \exp \left(-\frac{\theta_2}{T}\right) \exp \left(-\frac{\theta_3}{T}\right) \quad (4)$$

where the constant is truly a constant for any particular experiment.

When nitrous oxide decomposes the energy of decomposition is released and is converted to static kinetic energy and uniform kinetic energy of the gas. This heat addition produces a decrease in the density of the gas and an increase in the temperature. Thus, we find that the intensity of the radiating gas will vary both as the density changes, as the temperature changes, and as the amount of decomposing species changes. To interpret the radiation from the gas in such a manner as to obtain reaction rates we must consider all of these possible changes. In general, we may eliminate to a large extent the effect of changing density and changing temperature by using a large amount of some diluent. In other words, we may mix the gas which we are studying with an excess of argon or some other gas. In the experiments presented in the following sections the diluent was normally about 98% of the mixture. That is, the amount of nitrous oxide corresponded to 2% of the total mixture by volume. In this situation and if the study of the radiation is restricted to the initial decrease in the radiating species then the temperature and density will remain essentially constant and we may write for the intensity of the radiation

$$I = (\text{const.})_3 (C) \quad (5)$$

Thus we see that the radiation is directly proportional to the concentration of the radiating species which, in this case, is nitrous oxide.

In studying the radiation from nitrous oxide primary emphasis was placed upon the radiation at 4.5 or 3.9 microns. The radiation occurring at 4.5 microns corresponds to the fundamental of the anti-symmetric mode or upper valence bond of the nitrous oxide molecule. The radiation at 3.9 microns corresponds to the first overtone of the so-called symmetrical mode or lower valence bond of the nitrous oxide molecule. The reason for observing radiation at both points will be explained in a later section.

It was necessary to use sapphire windows, front-surfaced mirrors and an indium antimonide infrared detector to observe the radiation in this region of the infrared. A Perkin-Elmer Model 98 monochromator was used

to provide the necessary isolation of the wave length region of interest. The optical arrangement used in this experiment is shown in Figure 4. The response time of the infrared detection system was found to be less than 1 microsecond.

D. Gas Preparation

The diluents chosen in these experiments were argon, oxygen, nitric oxide, and air. Argon was chosen for two primary reasons; 1.) the use of argon as a driven gas containing about 2% nitrous oxide makes it possible to obtain the necessary Mach numbers rather easily, 2.) with argon the decomposition of nitrous oxide would be a true decomposition process rather than a bimolecular chemical reaction. The use of nitric oxide as a diluent was selected because of the possible role of nitric oxide in the decomposition mechanism during decomposition of nitrous oxide. Oxygen was chosen for the same reason. Several experiments were conducted using air as the diluent to determine the effect of air on the decomposition of nitrous oxide such that estimates could be made of the decomposition rate of air-nitrous oxide mixtures in the stagnation chamber of hypersonic wind tunnels. All gases, except air, were obtained from the Matheson Company. The argon was specified by Matheson to have a minimum purity of 99.998% with the main impurity being nitrogen. This purity was checked with the gas chromatograph facility at the Rocket Research Laboratory and found to agree quite well with the Matheson estimate. The only other purification procedure involved the use of askerite to remove the polyatomic molecules, except nitrous oxide, and Drierite to remove moisture from the gases. It was found that a fair amount of nitrogen dioxide existed in the nitric oxide. However, passage of the nitric oxide through the askerite removed this impurity.

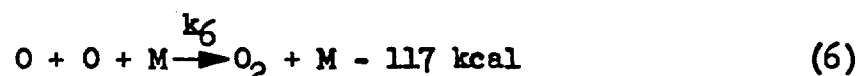
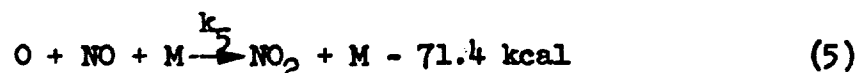
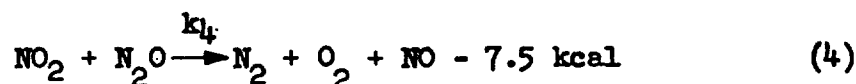
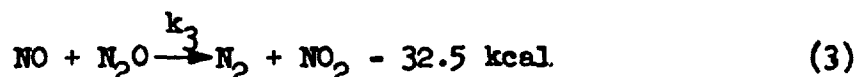
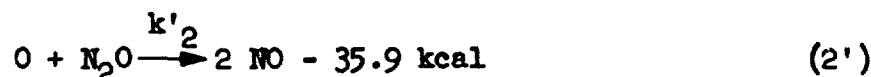
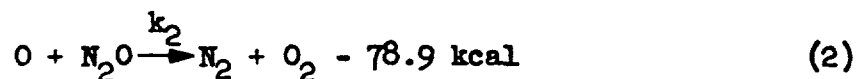
Nitrous oxide and the diluent were premixed in a special mixing chamber which was provided with paddle wheels to insure uniform mixing. The percentage of nitrous oxide in the mixture was generally about 2% in all cases except the initial experiments with argon reported in Ref. 7. In general, the percentage of nitrous oxide varied between 1.9 and 2.1 per cent with a nominal average of 2%. This percentage was determined by use of the gas chromatograph. Several samples were taken both at the beginning, after the gases were mixed, and just before the mixing chamber was emptied. The samples taken before and after use of the mixed gas agreed quite well. Because of the high pressure in the mixing chamber, about 300 psi, once the gas had been premixed it could be used for many experiments.

SECTION III

DETERMINATION OF THE REACTION RATE CONSTANT

The basic reactions which must be considered in studying the rate of decomposition of nitrous oxide are usually considered to be

Reaction



To determine the combined effect of all of the various reactions in the decomposition of nitrous oxide in one particular study would be almost completely hopeless. However, some insight may be obtained by studying: 1.) the initial rate of decomposition in which only reaction 1 is of importance, 2.) the effect of nitric oxide on the decomposition of nitrous oxide, and 3.) the effect of the other reaction products on the rate of decomposition of nitrous oxide. Reaction 2 involving the reaction between atomic oxygen and nitrous oxide is somewhat difficult and has not been considered in this study.

The true thermal decomposition of nitrous oxide is only achieved during the initial stages of the decomposition. After the nitrous oxide has started to decompose the nitrous oxide molecule begins to react with the decomposition products. Hence, the result would not be a true thermal decomposition. If we consider only the initial steps of the decomposition then we may consider the reaction to be





In these reactions species M is considered to be any molecule capable of producing an excited state in the nitrous oxide. The excited state or activated complex is discussed in considerable detail by Slater (Ref. 15). In the concept of the activated complex it is assumed that the energy of the molecule is increased to a point at which the molecule is considered to be in an excited state. The molecule subsequently undergoes a decomposition from the excited state into the reaction products. In the case of nitrous oxide the activated complex is represented by N_2O^* . The first of the two equations above gives the rate of activation and deactivation of the activated complex due to collisions with species M. The second of the two equations gives the rate of decomposition of the activated complex. If we assume, as is usually the case, that the concentration of activated species is maintained at a relative equilibrium value then the rate of decomposition of nitrous oxide may be given as

$$\frac{d(\text{N}_2\text{O})}{dt} = - \frac{(\text{N}_2\text{O}) (M) k_a}{1 + (k_a/k_1) (M)} \quad (8)$$

We may further write this expression as

$$\frac{d(\text{N}_2\text{O})}{dt} = - K_{\text{exp}} (\text{N}_2\text{O}) \quad (9)$$

where K_{exp} (for experimental) is the experimentally determined rate constant based on a first order reaction. We may relate this experimentally determined rate constant to the rate of decrease of the intensity of the infrared radiation by using equations (5) and (9).

Thus we find that the reaction rate constant for a first order reaction may be given as

$$K_{\text{exp}} = - \frac{\ln \left(\frac{I}{I_0} \right)}{(t - t_0)_L} \quad (10)$$

where I/I_0 is the ratio of the intensity at a time $(t - t_0)$ after the shock wave to the intensity of the radiation immediately after the shock wave. To determine the true thermal decomposition of the nitrous oxide it is necessary that we determine K_{exp} in the initial phases of the decomposition.

Hence, we are particularly interested in the initial intensity decrease after the arrival of the shock wave.

Because the incident shock wave is used in the experiments, it is necessary to multiply the oscilloscope or laboratory time by the density ratio across the shock wave to obtain the so-called gas time or the actual time during which the gas has been at a certain temperature. In this manner we obtain for the first order reaction rate constant the expression

$$K_{\text{exp}} = - \ln (I/I_0)/(\rho_2/\rho_1) (t - t_0)_L \quad (11)$$

Since we know the conditions of the gas immediately behind the shock wave, we may determine the reaction rate constant both for a particular concentration and temperature, or pressure and temperature. It is generally best to consider the variables concentration and temperature since the concentration gives a better indication of the collision frequency than does the pressure.

We may express the first order reaction rate constant as

$$K_{\text{exp}} = A \exp (- E_{\text{act}}/RT) \quad (12)$$

where A is the frequency factor and E_{act} is the activation energy. Taking natural logarithms of both sides we obtain

$$\ln K_{\text{exp}} = \ln A - \frac{E_{\text{act}}}{RT} \quad (13)$$

Thus, if we plot the value of the natural logarithm of K_{exp} vs. the inverse of the temperature for a constant concentration, applying a constant frequency factor, then the resulting curve should be a straight line with a slope given by $- E_{\text{act}}/R$. Therefore, if the experimental data are presented in this manner and the activation energy is determined for various concentrations, then some indication as to the reaction mechanism may be obtained for the particular system under consideration. The elementary considerations of the unimolecular reactions have been given by Slater (Ref. 15). For more details concerning the experimental determination of the activation energy and the frequency factor the reader is referred to Ref. 15. In general, all of the data presented in the following section will be based on the equation above.

SECTION IV

MEASUREMENTS

In this section we shall present the experimental data obtained during the present study. We shall be concerned only with the results obtained and

leave the subsequent evaluation of these results to the next section. In this manner we can bring all the results together and form a complete picture of the thermal decomposition of nitrous oxide.

A. Argon-Nitrous Oxide Mixtures

Most of the experimental results obtained in this study were obtained with argon as the diluent. In this manner we may study the thermal decomposition of nitrous oxide without any side effects due to possible reactions. It will be shown later that the reaction between nitric oxide and nitrous oxide does not necessarily lead to a thermal decomposition of nitrous oxide. It was particularly convenient to use argon since the density ratio across the shock wave in argon is rather low, being between 3.5 and 3.9. This means that the actual gas time was only 3.5 to 3.9 longer than the time displayed on the oscilloscope. This longer time gives us a better time resolution during the initial stages of decomposition.

The concentration of the argon-nitrous oxide mixtures varied from a low concentration of about 0.07×10^{-4} moles/cc to a maximum of 5.9×10^{-4} moles/cc. These two extremes in concentrations correspond to extremes in pressures ranging from 1 atmosphere to 80 atmospheres. By examining the variation of the reaction rate constant with concentration we may obtain an insight into the mechanism of the decomposition of nitrous oxide.

The reaction rate constants as plotted against the inverse of the temperature for the argon-nitrous oxide mixtures are given in Figure 5. The legend shows the various concentrations. The activation energy for the concentrations increased with increasing concentration from a low value of 49,500 calories per mole to a maximum of 56,000 calories per mole for the concentration of 1.5×10^{-4} moles/cc. A graph of the reaction rate constant versus concentration is shown in Figure 6. From this figure we find that the change of the rate constant with concentration is beginning to level off at the higher concentrations although, at this point, we cannot find the maximum or final value of the activation energy for an infinite concentration.

B. Nitric Oxide-Nitrous Oxide Mixtures

The role of nitric oxide in the decomposition of nitrous oxide has been postulated by several individuals to be quite important. The data obtained in the experiments are shown in Figure 7 and cover a concentration range from 0.08×10^{-4} moles/cc to a maximum concentration of 0.304×10^{-4} moles/cc. We find that the data may be fitted by a straight line fairly well. The activation energy obtained for the three lines shown on the figure was very close to 50,000 calories per mole.

C. Oxygen-Nitrous Oxide Mixtures

The data obtained in the oxygen-nitrous oxide mixtures cover a concentration range of 0.11×10^{-4} moles/cc to 0.39×10^{-4} moles/cc. In general, the data could be fitted fairly well by a straight line.

The slope of the straight line increased slightly at higher concentrations. The activation energies for the two lines shown in Figure 8 are 48,300 calories per mole and 50,000 calories per mole. In general, the rate of decomposition of nitrous oxide was only slightly faster in oxygen than in argon.

D. Air-Nitrous Oxide Mixtures

Several experiments were obtained with air as the diluent. These experiments covered a concentration range from 0.07×10^{-4} moles/cc to 0.41×10^{-4} moles/cc. The data could be fit fairly well to a straight line, however, slightly more scatter was experienced in these experiments than in the experiments with oxygen-nitrous oxide, nitric oxide-nitrous oxide and argon-nitrous oxide mixtures. The data presented in Figure 9 and represented by the two straight lines lead to activation energies of 50,000 calories per mole and 52,000 calories per mole. In general, the reaction rate in air was slightly faster than the reaction rate in oxygen.

E. Pure Nitrous Oxide

The experiments conducted with pure nitrous oxide provided some rather interesting results. According to theoretical calculations the shock wave velocity in pure argon is somewhat higher than that in pure nitrous oxide for identical conditions in both the driver and the driven sections. Experimentally, it was found that under these conditions the shock wave velocities in argon were sometimes higher and sometimes lower than those in nitrous-oxide. They were hardly ever equal to each other. The velocities obtained are shown in Figure 10. That the shock wave velocities in nitrous oxide were lower than those in argon can be explained on the basis of the high number of internal degrees of freedom possessed by nitrous oxide. No reason can be given why the wave velocity in nitrous oxide can be higher than that in argon unless we assume that a rapid decomposition of the nitrous oxide occurs.

To investigate the possibility of an appreciable decomposition of nitrous oxide in the wave which might lead to a detonation wave attempts were made to detonate this gas in a 180 foot detonation tube. Several methods were used to establish a detonation wave. The exploding wire technique produced no detonation waves. Even shock waves of moderate to high strength were ineffective. Although no stable detonation waves were formed, it appeared that some decomposition occurred because brown fumes appeared in the shock tube.

Another rather interesting result was the wave form of the output of the radiation from the decomposing gas. It was shown in Section III that the radiation output from nitrous oxide in an excess of argon was quite smooth and gave a uniform decomposition rate which is to be expected. However, in pure nitrous oxide the radiation pattern was quite uneven; it is shown in Figure 11. These types of radiation patterns were not just accidental but were consistently obtained with pure nitrous oxide. Several attempts were made to determine the cause for this radiation pattern and none were fruitful. If it is assumed that the shock wave is spinning, as in a spinning detonation, a radiation pattern similar to the one observed may be obtained.

As a further aid in the analysis of the shock wave in pure nitrous oxide, the radiation in the visible region was studied. However, even in the visible region around 5900 Å the radiation pattern exhibited a similar type of intensity variation. A typical trace of the radiation output is shown in Figure 12.

SECTION V

DISCUSSION

A. Nitric Oxide-Nitrous Oxide Mixtures

The rate of decomposition of nitrous oxide in an excess of nitric oxide was determined on the basis of a first order reaction according to equation 6. Unfortunately, it is impossible with the amount of data collected to decide whether the nitric oxide-nitrous oxide decomposition is a bimolecular or a monomolecular reaction. According to our experiments it appears that the reaction is bimolecular. Kaufman and Kelso (Ref. 16) have determined the rate of nitrous oxide decomposition in nitric oxide and find that the reaction is bimolecular. According to these authors the reaction is given by

$$k_3 = 2.5 \times 10^{14} \exp \left(- \frac{50,000}{R T} \right)$$

If we assume that the reaction studied in this particular research program was also bimolecular then our rate constant may be given as

$$k_3 = 2.0 \times 10^{14} \exp \left(- \frac{50,000}{R T} \right)$$

The frequency factor in our expression represents an average value obtained from experiments with various concentrations which produced values ranging from 2.5×10^{14} to 1.7×10^{14} .

B. Argon-Nitrous Oxide Mixtures

The rate of decomposition of nitrous oxide in argon has been determined over a great range of concentrations. Therefore, it is possible to establish the relationship between the rate of decomposition and concentration for this reaction. The results are given in Table I. It is seen that the activation energy increase from 49,000 cal/mole at a concentration of 0.13×10^{-4} moles/cc to 56,000 calories/mole at a concentration of 1.5×10^{-4} moles/cc. This relationship is shown graphically in Figure 13. Since the highest concentration used in these experiments amounted only to 1.5×10^{-4} moles/cc, it is impossible to extrapolate the curve in Fig. 13 to determine the activation energy E_∞ at the high concentration limit. All that can be said is that the value of 60,000 cal/mole for E_∞ by Johnston (Ref. 4) does not contradict the values shown in Fig. 13.

According to Slater (Ref. 15) for a unimolecular reaction the activation energy increases with concentration. The activation energy has its lowest value when the concentration is very small. Fig. 13 is in agreement with this prediction.

To determine the activation energy for the second order reaction in which the activated nitrous oxide molecules are formed we make use of the following relationship.

$$\frac{K_{exp}}{(M)} = k_a - K_{exp} \frac{k_a}{k_1} \quad (14)$$

This equation takes into consideration the fact that at constant temperature K_{exp} depends on the concentration (M). When, for a given temperature, the values of $K_{exp}/(M)$ are plotted versus K_{exp} we obtain a curve whose slope represents the ratio k_a/k_1 as a function of the concentration.

The rate constant k_a was determined for concentrations ranging from 0.13 to 0.28×10^{-4} moles/cm³. In figure 14 the logarithm of $k_a \times T^{-1/2}$ is plotted versus the inverse of T. According to the general expression for a bimolecular reaction rate constant

$$k_a = BT^{1/2} e^{-\frac{E_{act}}{RT}} \quad (15)$$

this curve should be a straight line whose slope represents the quantity E_{act} . According to our data the activation energy amounts to 41,700 calories per mole within 1,000 calories. Thus the rate constant can be written as

$$k_a = 2.8 \times 10^{11} T^{1/2} \exp\left(-\frac{41,700}{RT}\right) \quad (16)$$

The activation energy in equation (16) represents an average value because the activated molecules may consist of several energy levels from which they can dissociate. In view of the fact that 38,300 calories per mole are required to break the N-O bond in the nitrous oxide molecule, an activation energy of 41,700 calories per mole appears to be reasonable.

C. Oxygen-Nitrous Oxide

At 1900°K for a concentration of 0.14×10^{-4} moles of gas mixture per cubic centimeter the nitrous oxide decomposition in oxygen (2% nitrous oxide, 98% oxygen) is approximately 40% faster than in argon (2% nitrous oxide, 98% argon). Since oxygen is a diatomic molecule it can transfer energy to the nitrous oxide more readily than the argon atoms. There is no reason to assume that the decomposition in oxygen is a bimolecular reaction.

Based on the assumption that the decomposition of nitrous oxide in oxygen is also governed by a monomolecular reaction the rate constant for this reaction has also been calculated for a first-order reaction. The result is given in Table 1.

D. Air-Nitrous Oxide

Because of their possible use in hypersonic wind tunnels nitrous oxide-air mixtures were studied extensively. It was found that the decomposition of nitrous oxide in air is approximately 30% faster than in oxygen. Although the air was dried before it was used, a small amount of water vapor may still have been in the air. Therefore, the actual reason for the slightly higher decomposition rate of nitrous oxide in air cannot be given at this time.

E. Further Attempts to Determine the Mechanism of the Decomposition of Nitrous Oxide.

It has been postulated by Lindars and Hinshelwood (Ref. 17) that the decomposition of nitrous oxide occurs from an excited electronic energy level of the molecule. The ground electronic state of nitrous oxide is a $^1\Sigma$ state. If decomposition into nitrogen and atomic oxygen occurs from this level the resulting oxygen must be in an excited electronic energy level. However, the decomposition occurs from a triplet state the oxygen would be in its ground electronic state. If the atomic oxygen formed during the decomposition is in an excited electronic energy level then, in principle, we should be able to detect the radiation from the transition to the ground electronic state. Unfortunately, the radiation life time of the excited oxygen is 110 seconds for the 1D state (Ref. 18). In the laboratory it would be impossible to detect the radiation emitted in the transition to the ground state. However, it was thought that it may be possible to introduce into the gas an atom which would exchange electronic energy with the oxygen in such a way that a resonant exchange occurs and the excited additive atom would then radiate. Such an atom could be sodium. Sodium was chosen since the energy level for obtaining the sodium D lines is about 2.09 electron volts, while the energy level of the 1D state is 1.97 electron volts.

To obtain the sensitized fluorescence of sodium the chloride of this element was introduced into the gas mixture in the shock tube. The yellow D lines, however, could not be detected in the radiation. It may have been too weak to appear besides the very intense radiation from nitrogen dioxide which has very strong bands in this spectral region. When added to pure argon, sodium chloride produced the yellow D lines in the shock wave as a result of thermal excitation. However, this radiation was found to be very weak so that it would not be detectable in the presence of the nitrogen dioxide spectrum. Further experiments are necessary to develop means which definitely would establish the presence or absence of electronically excited atomic oxygen in the reaction zone of decomposing nitrous oxide.

SECTION VI

ACCURACY OF MEASUREMENT

The accuracy of measured reaction rate constants depends greatly on the purity of the gas mixtures used for the experiments. To minimize these effects the gases were carefully purified before use and the shock tube was cleaned as frequently as deemed necessary. Apparently contamination from experiment to experiment was negligible: it was found that occasional omission of the cleaning operation did not affect the results.

Systematic errors may arise from (1) the method of calculating temperature and pressure behind the shock wave, (2) the infrared detection system used to monitor the nitrous oxide concentration in the shock wave, and (3) from the uncertain effect of the boundary layer built-up behind the shock wave.

Because of the small percentage of nitrous oxide in the mixtures with argon the assumption of thermodynamic equilibrium behind the shock front will lead to very accurate predictions of temperature and pressure in these mixtures. When diatomic gases such as oxygen, nitric oxide, or air are used the temperatures in the shock front based on equilibrium calculations is slightly lower than the actual translational temperature because the vibrational modes of the molecules are not excited as rapidly as the translational mode. However, this behavior can be disregarded since the effect of higher translational energy is cancelled by the lack of energy transfer by vibrating molecules. Vibrational relaxation behind the shock wave will have a great effect on the determination of the nitrous oxide concentration by means of measuring its infrared radiation in the region between 2 and 6 microns. Since dissociation can occur only after the vibrational modes have been excited and since the relaxation rates will differ for different modes, measurements in two different wave length regions will at least minimize, if not completely eliminate, the relaxation effects. Experiments up to temperatures where decomposition just begins to become noticeable showed that above 900°K no lag in attaining vibrational equilibrium occurred. Furthermore, the intensity of the radiation behind the shock wave corresponded to the value predicted from other measurements. Therefore, we believe that our results for the reaction rate constant of the nitrous oxide decomposition are not affected by vibrational relaxation.

To investigate the effect of boundary layer build up on the measurements, studies were made with pure nitric oxide in the driven section of the shock tube. In the temperature region used the decomposition of nitric oxide is extremely slow. Therefore, the radiation of heated nitric oxide at these temperatures should remain constant in the wave unless boundary layer effects would cause premature cooling of the gas. Our observations showed that the radiation remains constant. Therefore, we concluded that boundary layer effects were insignificant. This conclusion is in agreement with the fact that at the pressures we employed boundary layer effects should be negligible.

SECTION VII

CONCLUSIONS

According to our measurements nitrous oxide decomposes quite rapidly at temperatures above 1400°K . For pure nitrous oxide at 1500°K the half life is approximately 300 microseconds. Although electrical heaters can be operated at these temperatures, it is doubtful that they can be used in conjunction with nitrous oxide to obtain high enthalpy flows. Usually the heaters burn out when the decomposition of nitrous oxide begins because of the sudden increase in temperature. To eliminate this difficulty it is planned to heat a stream of nitrogen to as high a temperature as possible. The hot nitrogen would then be mixed with preheated nitrous oxide. It is hoped that upon mixing of the two jets decomposition of the nitrous oxide will occur and that it will be complete.

At temperatures above 2200°K the decomposition of nitrous oxide was found to be so rapid that accurate values of the rate constant would not be ascertained. At these temperatures the half life of the nitrous oxide becomes less than 20 micro-seconds.

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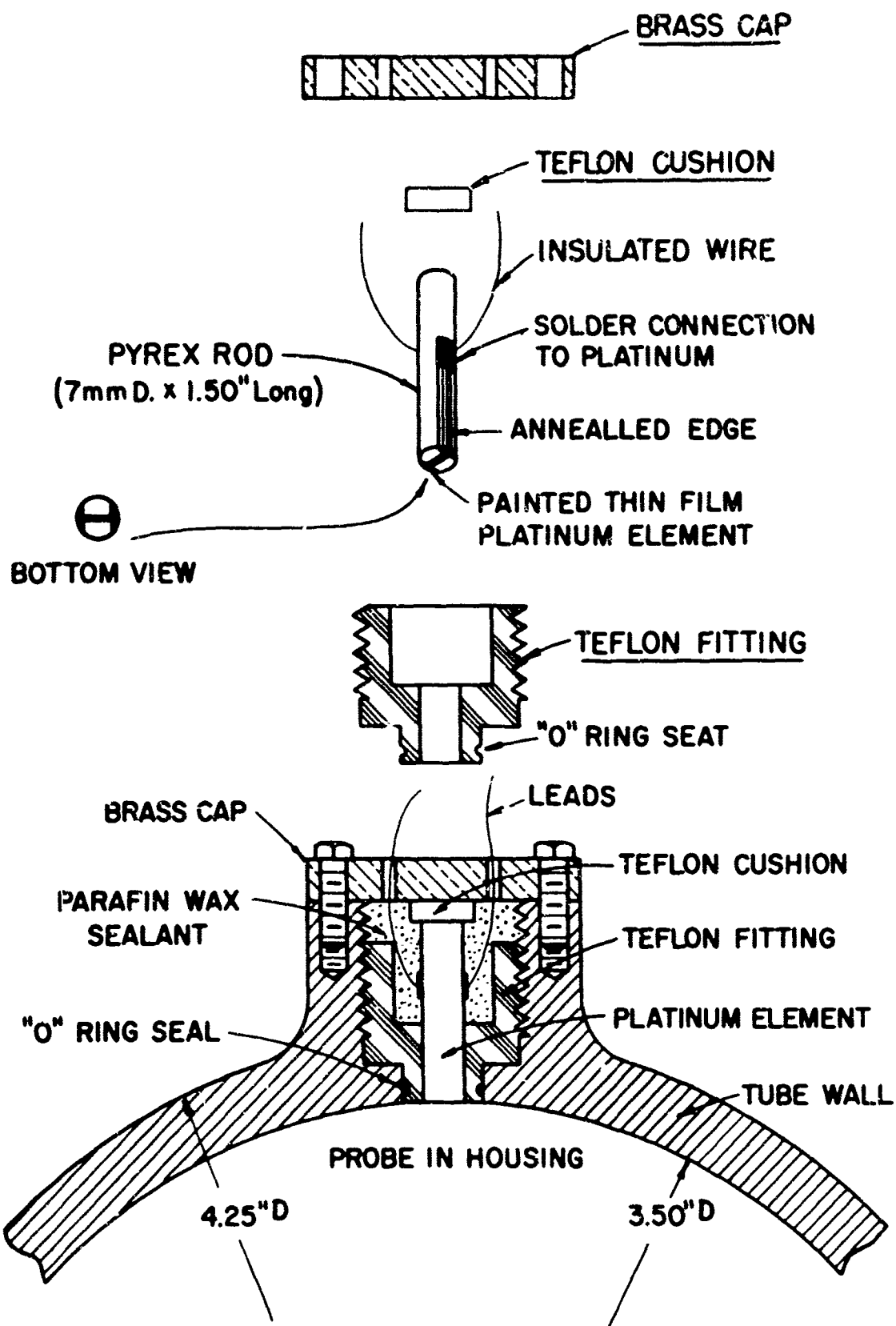
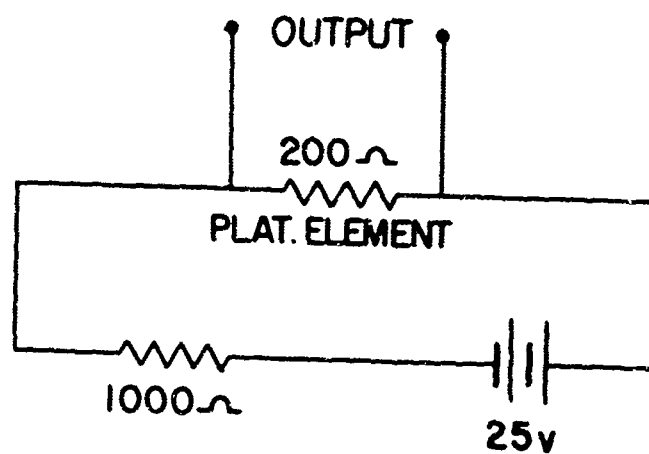


FIGURE 1. THIN FILM THERMOMETER PROBE



TYPICAL ONE TRANSISTOR AMPLIFIER

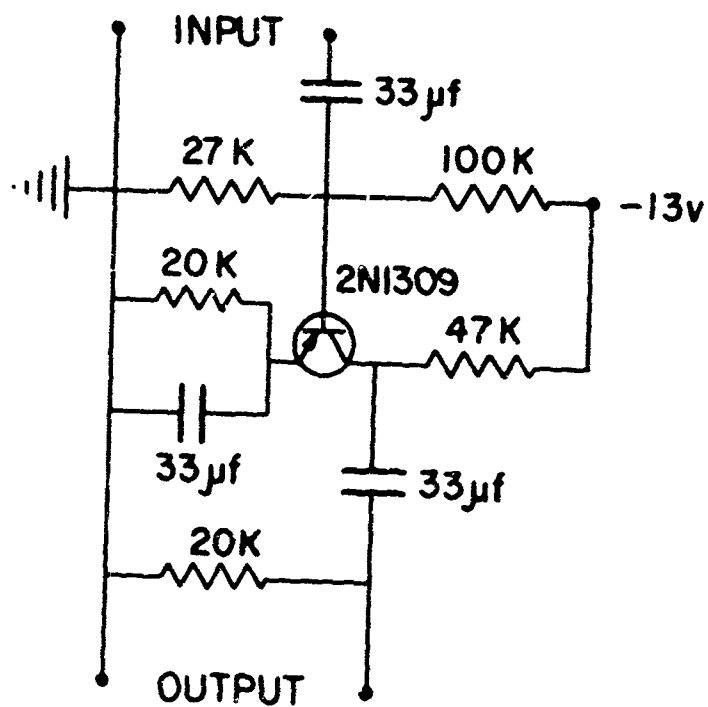


FIGURE 2. ELECTRICAL BRIDGE AND AMPLIFIER FOR PLATINUM ELEMENT

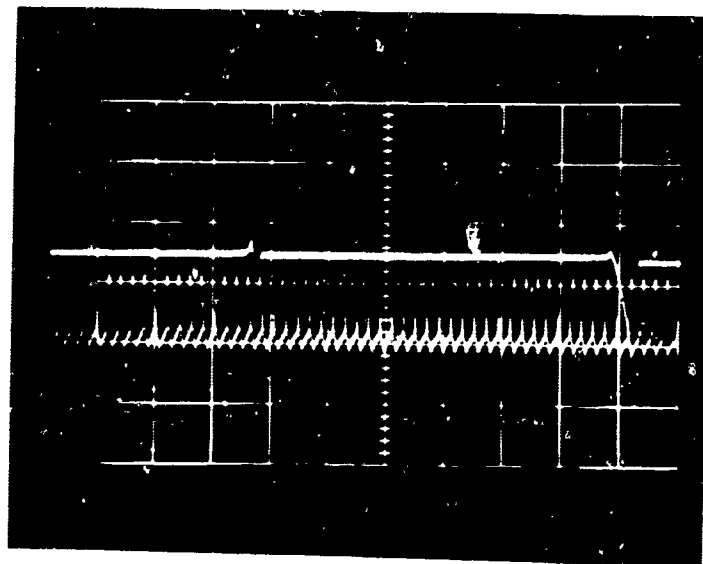


FIGURE 3. DIFFERENTIATED OUTPUT FROM PLATINUM STRIPS FOR VELOCITY MEASUREMENT (TIME IS FROM RIGHT TO LEFT), $50\mu s/DIV$

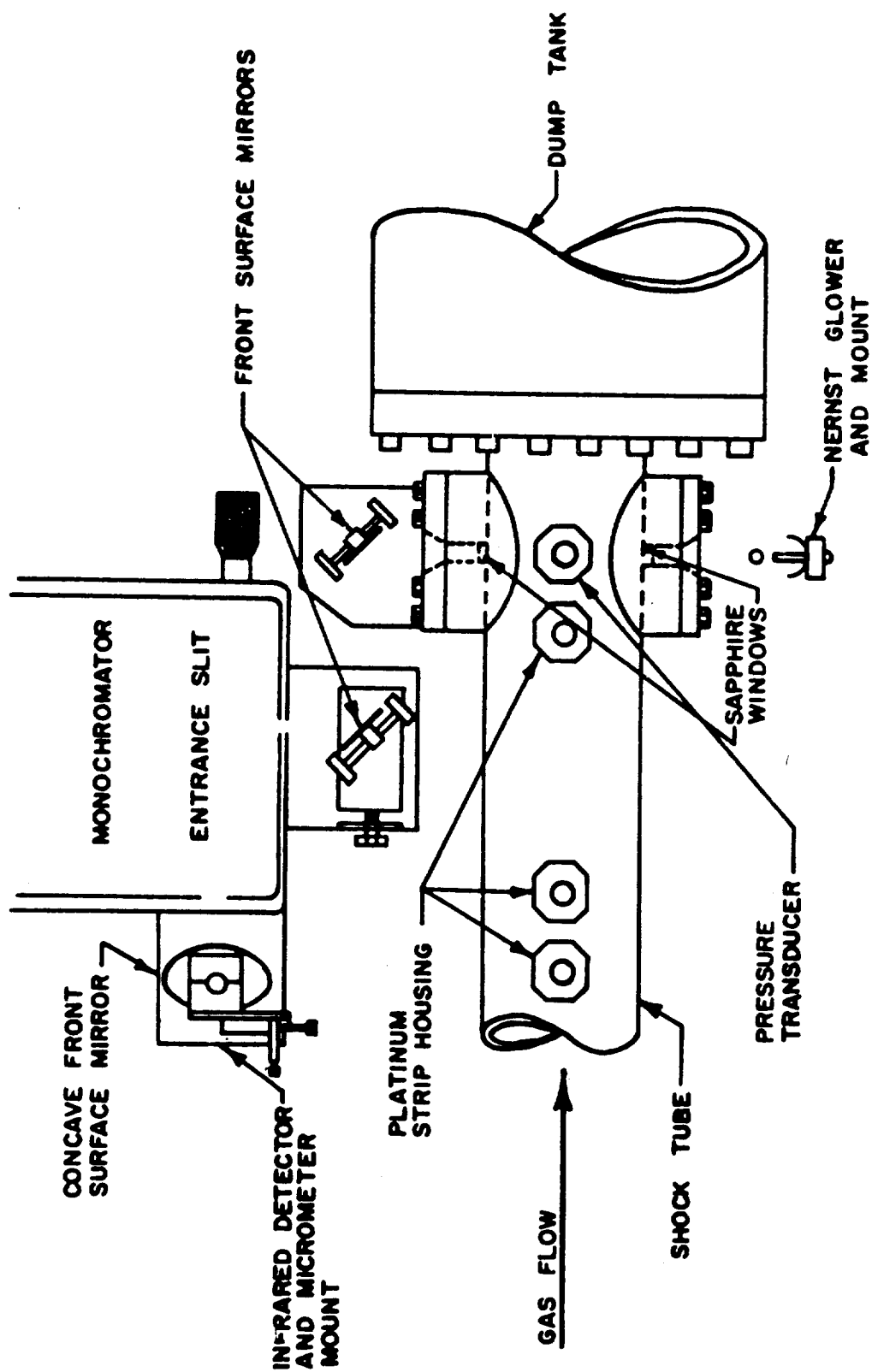


FIG. 4. INFRARED OPTICAL SYSTEM

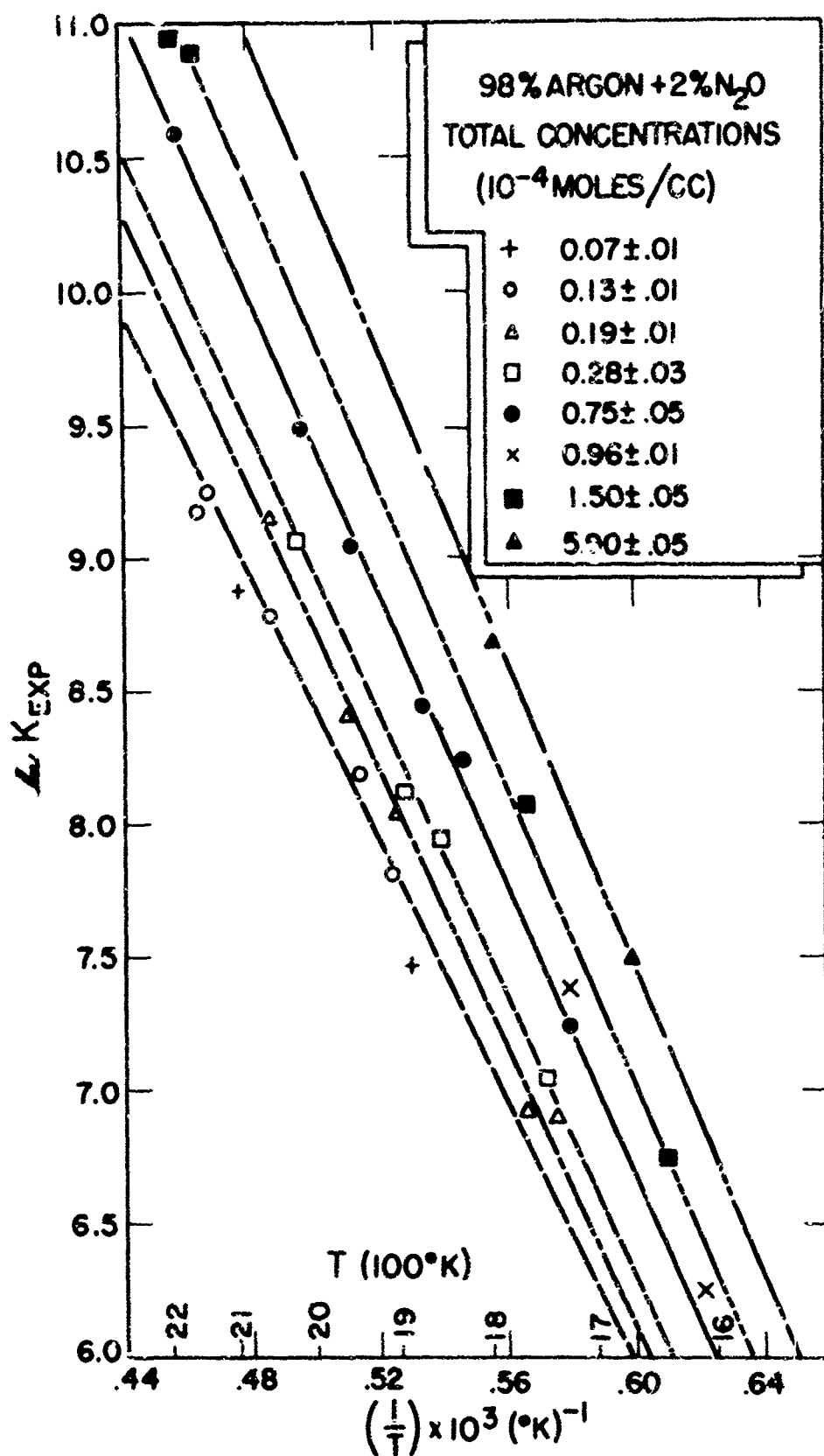


FIGURE 5. FIRST ORDER REACTION RATE IN ARGON-NITROUS OXIDE MIXTURES

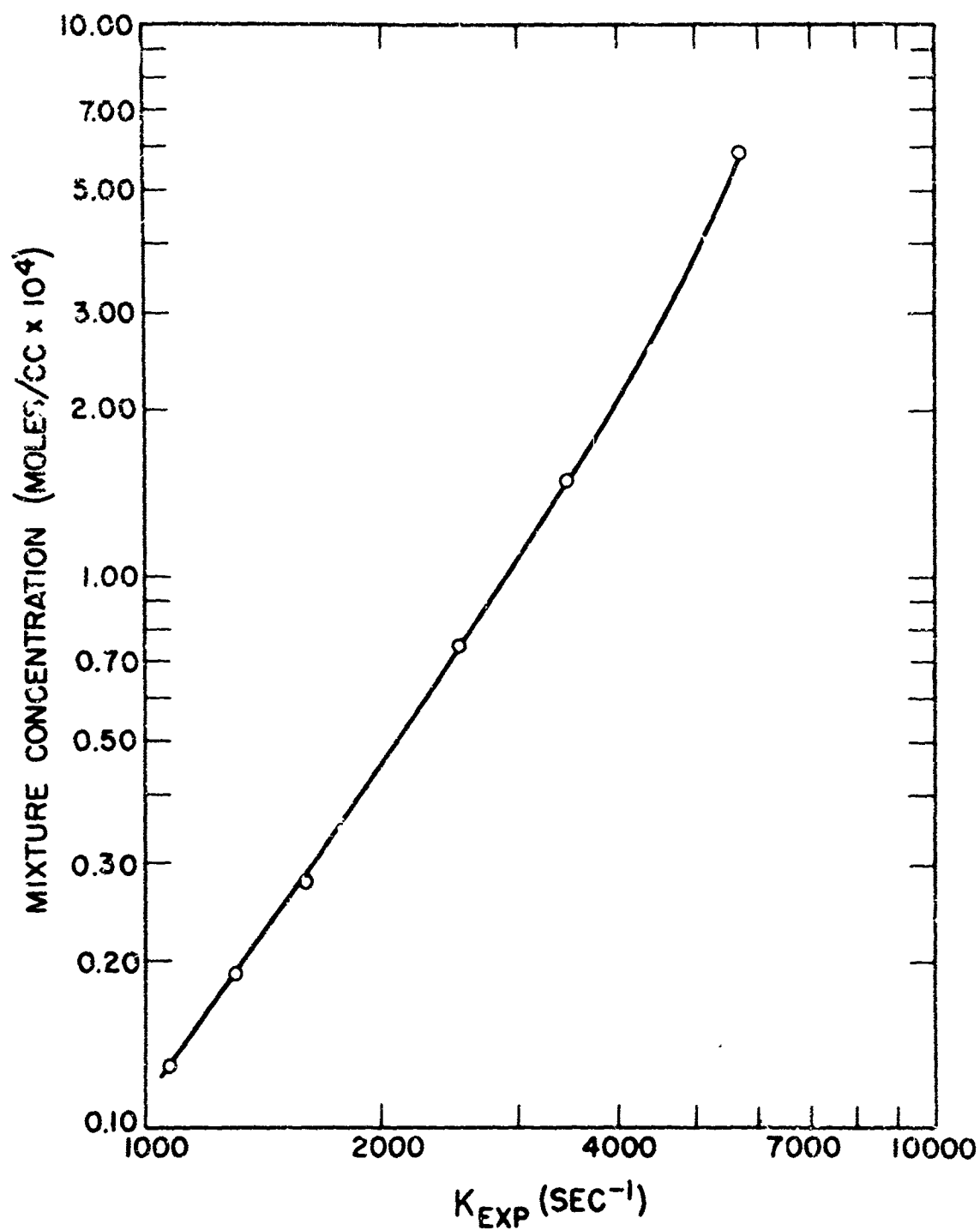


FIGURE 6. VARIATION OF FIRST ORDER RATE CONSTANT WITH CONCENTRATION IN 98% ARGON + 2% NITROUS OXIDE AT 1790°K

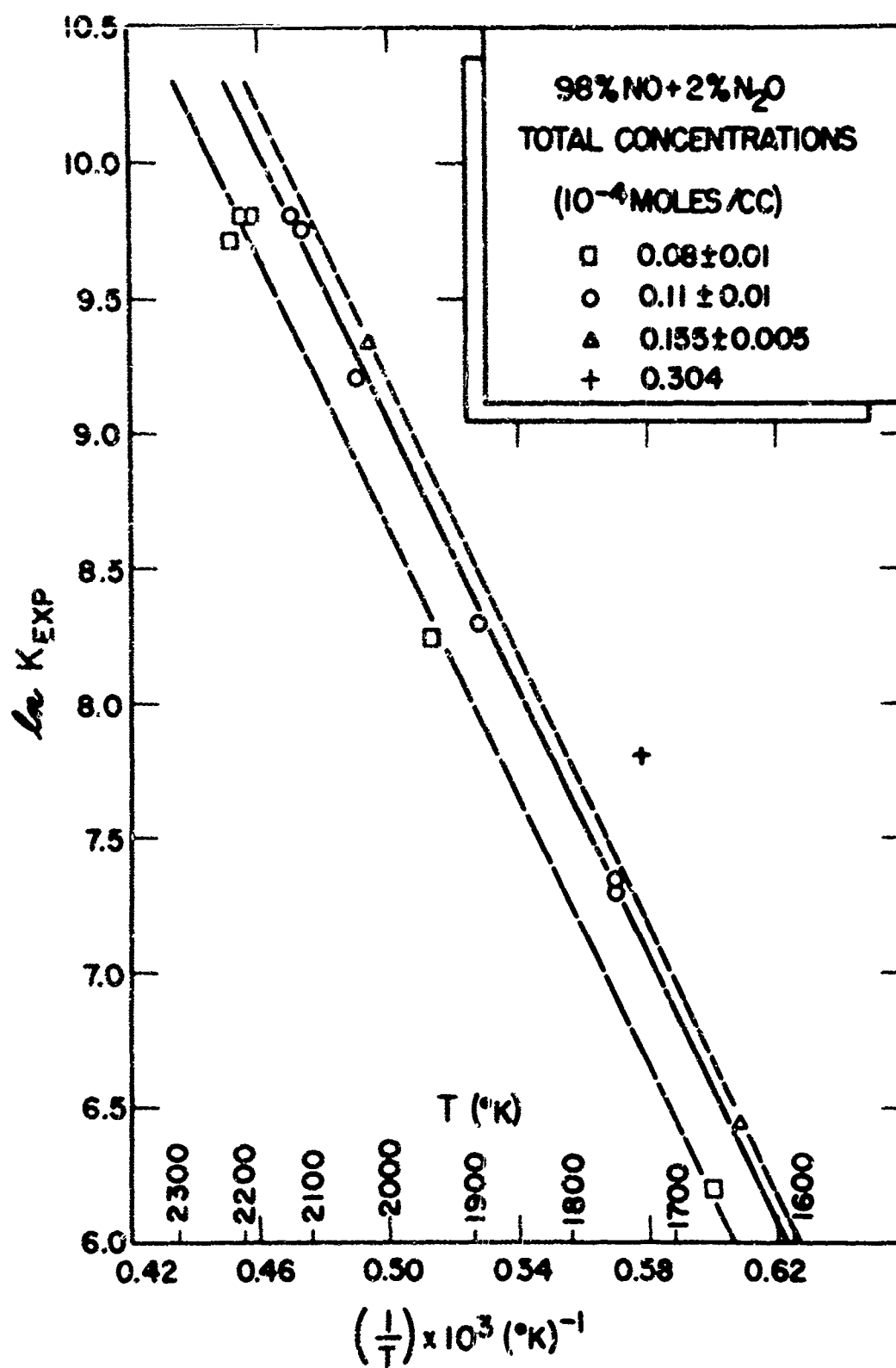


FIGURE 7 FIRST ORDER REACTION RATE CONSTANT IN NITRIC OXIDE-NITROUS OXIDE MIXTURES

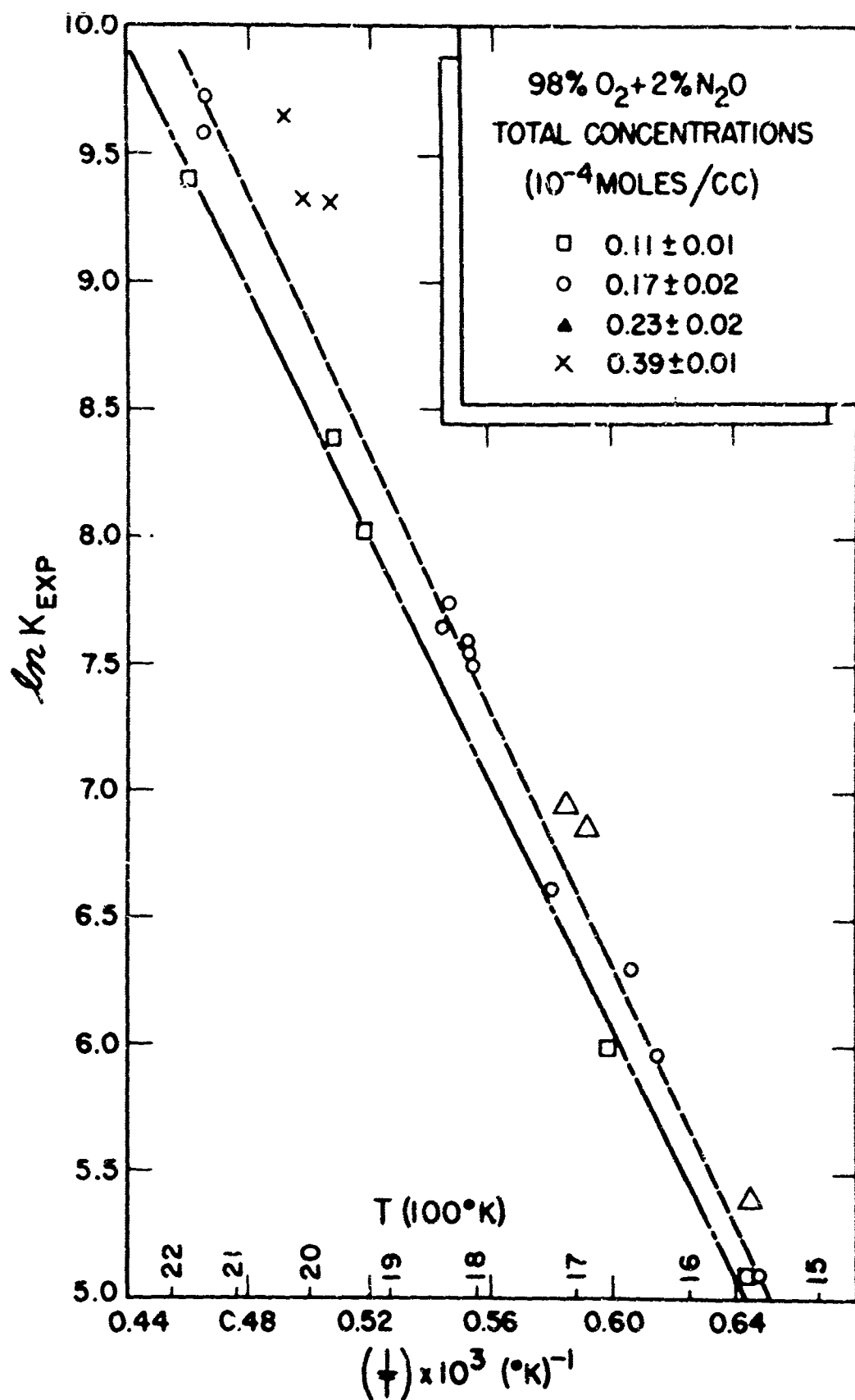


FIGURE 8. FIRST ORDER REACTION RATE CONSTANT IN OXYGEN-NITROUS OXIDE MIXTURES

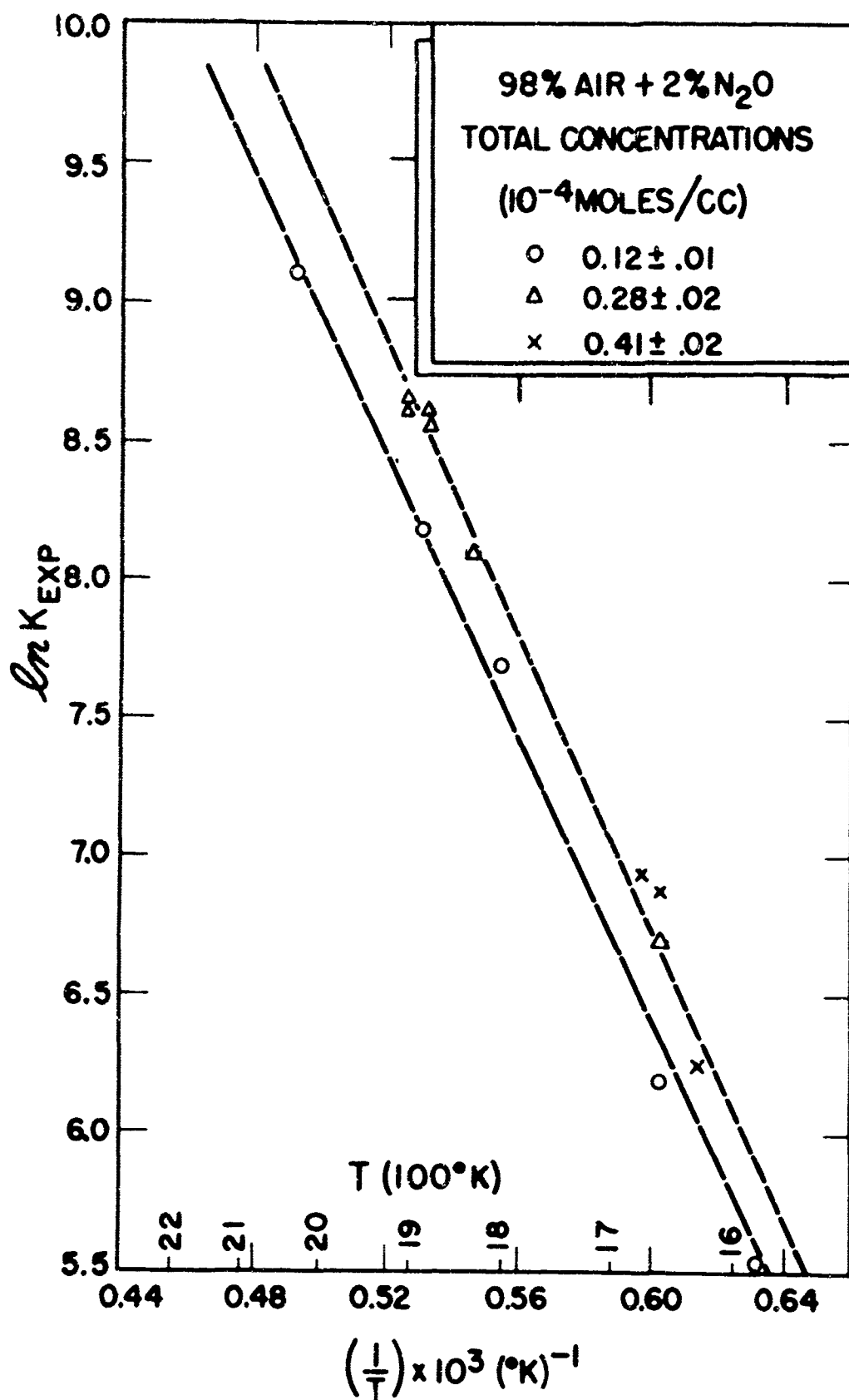


FIGURE 9. FIRST ORDER REACTION RATE CONSTANT IN AIR - NITROUS OXIDE MIXTURES

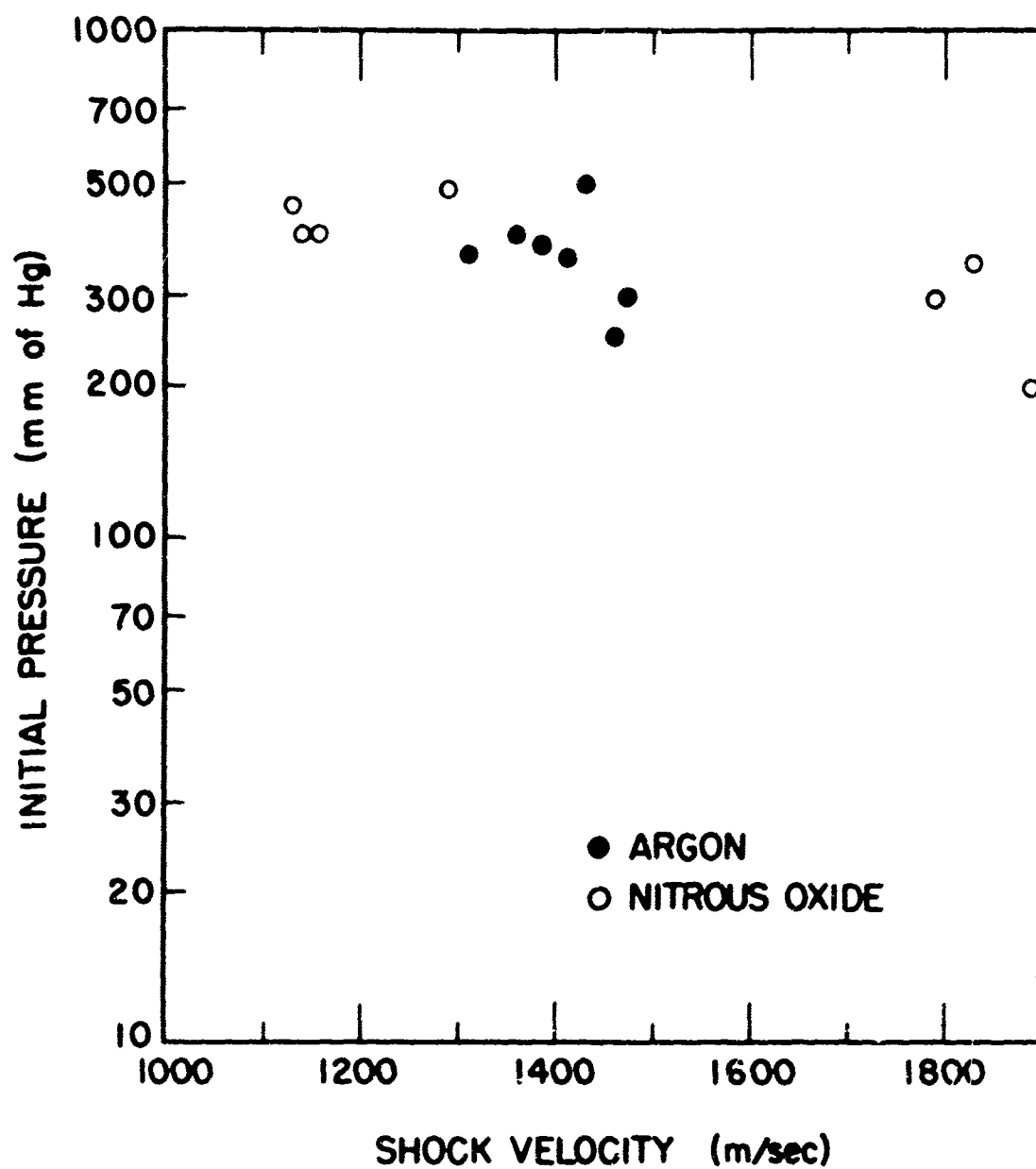
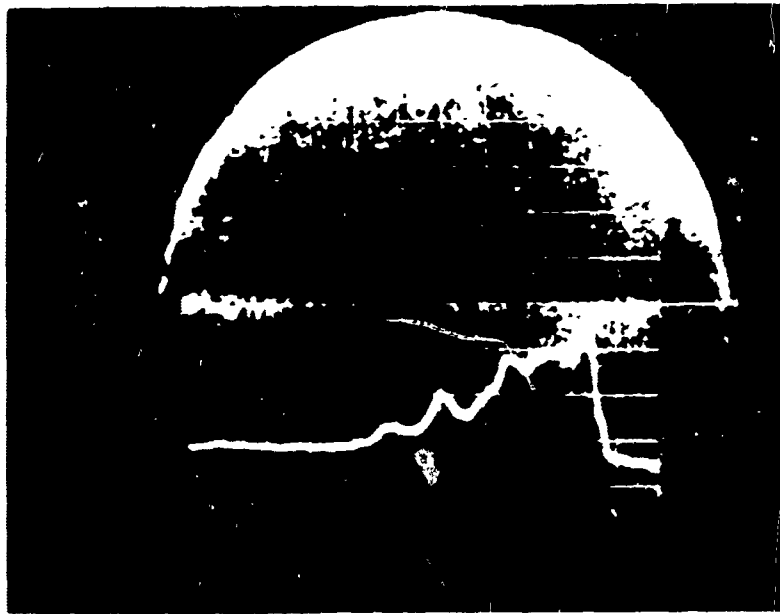


FIGURE 10. SHOCK WAVE VELOCITIES IN ARGON AND NITROUS OXIDE



**FIGURE 11 INFRARED RADIATION FROM SHOCK HEATED
100% NITROUS OXIDE (TIME IS FROM RIGHT
TO LEFT), $20\mu\text{s}/\text{DIV.}$, 1900m/s**



FIGURE 12. RADIATION FROM SHOCK HEATED 100%
NITROUS OXIDE AT 5900 Å (TIME IS
FROM RIGHT TO LEFT), 20 μ s/DIV., 1820 m/s

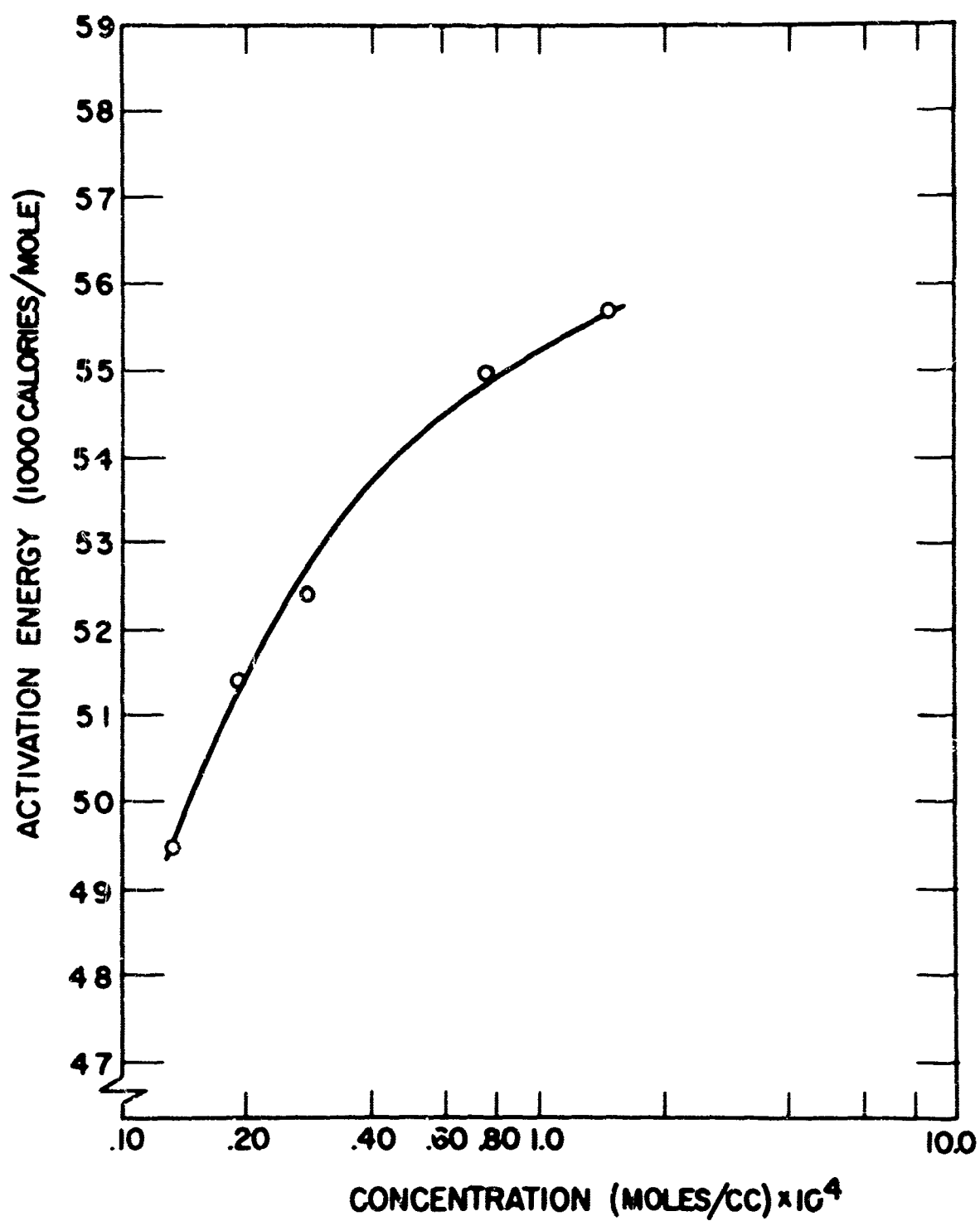


FIGURE 13. VARIATION OF ACTIVATION ENERGY WITH CONCENTRATION IN 98% ARGON + 2% NITROUS OXIDE

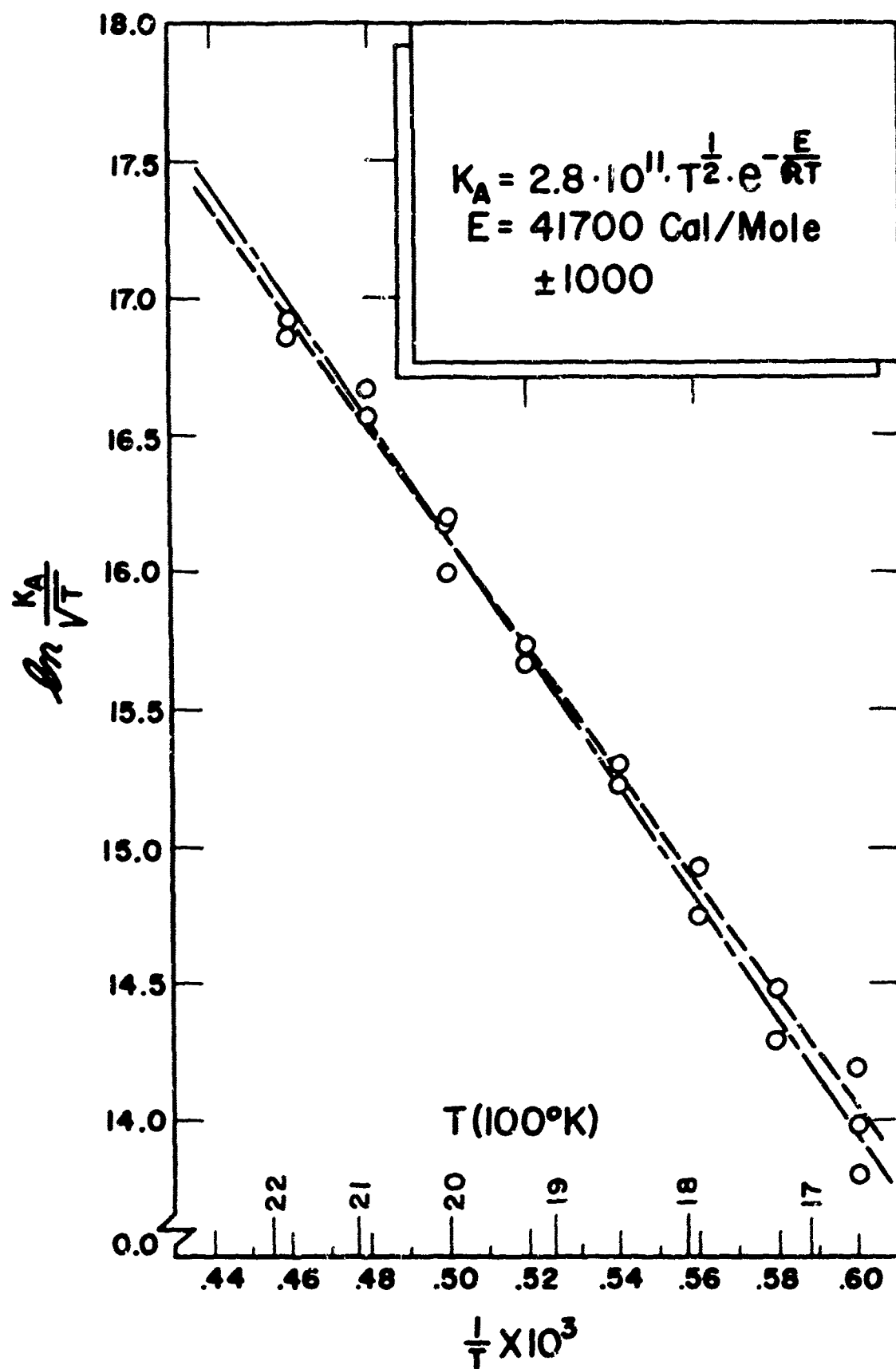


FIGURE 14. DETERMINATION OF THE RATE CONSTANT FOR EXCITATION

TABLE I
REACTION RATE CONSTANTS

Reaction	Concentration μ (Moles/cc) $\times 10^4$	Rate Constant
$\text{NO} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{NO}_2$	-	$2.0 \times 10^{14} e^{-\frac{50,000}{RT}} \text{ (Mole sec)}^{-1} \text{ cc}$
$\text{A} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} + \text{A}$	0.13	$1.28 \times 10^9 e^{-\frac{49,500}{RT}} \text{ sec}^{-1}$
	0.19	$2.63 \times 10^9 e^{-\frac{51,400}{RT}} \text{ sec}^{-1}$
	0.28	$4.1 \times 10^9 e^{-\frac{52,400}{RT}} \text{ sec}^{-1}$
	0.75	$1.26 \times 10^{10} e^{-\frac{55,000}{RT}} \text{ sec}^{-1}$
	1.50	$2.3 \times 10^{10} e^{-\frac{55,700}{RT}} \text{ sec}^{-1}$
$\text{O}_2 + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} + \text{O}_2$	0.11	$9.1 \times 10^8 e^{-\frac{48,200}{RT}} \text{ sec}^{-1}$
	0.17	$1.95 \times 10^9 e^{-\frac{50,000}{RT}} \text{ sec}^{-1}$
$\text{Air} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} + \text{Air}$	0.12	$2.2 \times 10^9 e^{-\frac{50,000}{RT}} \text{ sec}^{-1}$
	0.28	$5.8 \times 10^9 e^{-\frac{52,000}{RT}} \text{ sec}^{-1}$